THE CARBURIZATION OF STEELS OF "KRUPP" ANALYSIS

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THESIS

THE CARBURIZATION OF STEELS OF "KRUPP" ANALYSIS

Submitted in partial fulfilment of the requirements for the degree of

MASTER OF SCIENCE IN METALLURGY

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Approved by the Committee on Graduate Instruction.

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Ph. D.

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SYNOPSIS

Samples of four lots of steel containing between 1.75 and 3.79% nickel and between 0.73 and 1.72% chromium were carburized to obtain information on the factors affecting rates and depths of carbon penetration. A review of previous work on carburization and diffusion of carbon is presented, and the relative importance of factors affecting rate of carburization is discussed. It was found that initial grain size had a marked effect on rate of carburization of a steel, and that the variation in alloy content among the different lots of steel had a slight effect on respective rates of carburization.

INTRODUCTION

Few processes have received the attention of metallurgists over a longer period of time than that of carburization of iron and steel. The many variables which affect the process, as well as the differing objectives which have determined the procedures of the respective investigators, have prevented a complete understanding of the laws governing rates and depths of carburization.

It would be out of the question to do justice to, or even to tabulate, in a single paper, the many contributions to our knowledge of this most interesting subject. The review of the subject which precedes the description of the experimental work, therefore, will be restricted to an analysis of factors affecting rates and depths of carburization. It seems well worth while to direct attention to the importance of an understanding of the laws governing rates of diffusion in solid metals for this purpose, as well as to the factors peculiar to reactions in the gaseous medium, which force us to modify our concept of diffusion as a measure of rate of carburization.

THE PROCESS OF CARBURIZATION

The surface of a steel speciman is carburized by heating in the presence of a carburizing agent. The essential conditions for carburizing are: that the steel be heated to the austenitic range; the the initial carbon content of the steel be below the limit of solubility at the carburizing temperature; that the carburizing agent react with the iron in such a manner as to give up carbon to the latter.

In carburizing, then, there is a gaseous system which supplies a compound capable of carburizing steel. (The discussion of carburizing with liquids is omitted). There is also a solid system in which the carbon atoms /29/ (or the Fe_3C molecules /21/) diffuses away from the surface, because of the concentration gradient of carbon. At the boundary between the two systems, which may be referred to as the interface, the carburizing gas gives up carbon to the iron, as has been stated.

EQUILIBRIUM

Strictly speaking, equilibrium does not occur in the carburizing process, and every step should be analyzed in terms of rates of reaction. The gaseous system at a distance from the interface is practically in equilibrium, and if carbon is available, as in pack-carburizing, CO_2 will be reduced to CO until the pressures of these two gases are practically at equilibrium for the temperature existing. The solid system is likewise practically at equilibrium at a distance from the interface.

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TEMPERATURE AND ITS EFFECT ON RATE OF CARBURIZATION

The carburizing temperature affects the rate of carburization in various ways.

A high temperature increases rate of diffusion in the solid metal by its effect on the diffusion coefficient (equation 4); and affects the rate of reaction of carbon and iron at the interface. A high temperature also increases the concentration of carburizing gas in such processes as that of pack-carburizing.

The carbon content of the metal at the interface is less than the limiting solubility of the carbon in the metal, which depends on the temperature, as reference to the equilibrium diagram of the iron-carbon system will show. There is evidence /6/ that this solubility limit is approached quite closely in practice, but is in general not reached, by the metal at the interface.

From these considerations it appears that the relation between temperature and rate of carburization is a complex one, and data on the relation of these two variables appearing in the literature /6//26/, are most useful for predicting results of carburization. This type of information is less useful for analysis of variations in rates of carburization, especially in the case of pack-carburizing, because of the difficulty of making accurate corrections for temperature variations.

CARBURIZING MEDIUM AND ITS EFFECT ON RATE OF CARBURIZATION.

Houdremont /6/ reports that a powdered mixture of charcoal 60% by weight and 40% barium carbonate produces a deeper case at moderate carburizing temperatures than illuminating gas or a selected mixture of organic carburizing agents. The same work gives data on other

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Houdremont /7/ reports that a powdered mixture of charcoal 60% by weight and 40% barium carbonate produces a deeper case at moderate carburizing temperatures than illuminating gas or a selected mixture of organic carburizing agents. The same work gives data on other

carburizing agents which have even lower carburizing rates. For long carburizing times and temperatures above 950°C. the differences in the rates of carburization obtained under these different conditions become much less /6/, as the carbon concentration at the interface approaches the limit of solubility.

Bramley //26//27//28//29// reports that rate of carburization is greater with either pyridine, methyl cyanide, or ammonia added to CO than when CO is used alone. In each case increasing the rate of supply of the gas increased the rate of carburization. Temperatures from 800 to 1000°C., times from 5 to 40 hours, and rates of supply of gas from 7 to 30 liters per hour per sample, were used.

Comparison of this work of Bramley with that of Houdremont and Schrader /13/, shows that Charcoal 60% barium carbonate 40% gives as rapid carburization as pure CO if the rate of supply of CO is low, about 15 liters per hour for the conditions existing in Bramley's experiments.

Recent industrial experience /12/ demonstrates that under favorable conditions a combination of CO and hydrocarbon gas produces a higher rate of carburization than CO alone.

It is known that the rate of carburization using charcoal alone in the pack-carburizing process is relatively low.

On the basis of the above information we may conclude that the rate of carburization as measured by the depth of case is approximately proportional to the pressure of CO present. Langenberger /17/ determined this relation experimentally. However, if other carburizing gases are present as well as CO a rate of carburization higher than that obtained with CO alone is observed under some conditions.

It seems most reasonable to postulate that if more than one

carburizing gas is present the reactions in the gaseous state proceed more rapidly, so that more carbon can combine with the iron in a given time than would otherwise be the case.

Consider the reactions which take place in carburizing with carbon and an energizer /21/:

$$2\ CO + Fe = Fe_3C + Co_2 \qquad (1)$$

$$CO_2 + C = 2\ CO \qquad (2)$$

If some agent more active than carbon in reducing CO_2 to CO were present, it is reasonable to suppose that carburization would proceed at a more rapid rate.

The carbon content of the surface of the steel cannot be measured very accurately, and figures usually given are the carbon content of a very thin layer removed from the surface. The actual carbon content of the surface approaches the limit of solubility of the steel at the carburizing temperature, and depends on the relative rates of solution of carbon and of diffusion of carbon. If the rate of solution of carbon is relatively low, the carbon content of the surface will likewise be low. For high temperatures and long carburizing times, changing the carburizing medium has relatively little effect on the carbon concentration at the surface and on case depth. /6/

THE CONSTITUTION AND STRUCTURE OF THE STEEL AND ITS EFFECT ON RATE OF CARBURIZATION.

The rate of carburization may be expected to vary with the alloy content of the steel. The limit of solubility of carbon in a steel at a given temperature will vary with the alloy content. Furthermore, it is to be expected that rates of diffusion in different alloys will vary. Houdrement and Schrader /13/ have determined the variation in rate of carburization when up to 6% of an alloying element has been

added to steel. A number of common alloying elements were so added, and in most cases the rate of carburization was thereby decreased. Houdremont /6/ has determined that the carbon content within 0.05 m.m. of the surface of several steels when carburized under similar conditions varied as follows: Nickel-chromium steel highest, nickel steel next, carbon steel lowest.

The thickness of the case is dependent on the rate of diffusion of carbon in the metal.

Diffusion of metals in the solid state obeys Fick's law: /22/:

$$Dm = D\,A\,\frac{(dc)}{(dx)}\,dt \qquad (3)$$

Where a mass dm of a substance diffuses across an area A in time dt.

dc/dx is the concentration gradient of the diffusing substance, where c is concentration, and x is distance from the interface of the solute metal.

D is the diffusion coefficient, which has been calculated by the Dushman-Langmuir equation as:

$$\log_e D = \log_e \frac{QS^2}{Nh} - \frac{Q}{RT} \qquad (4)$$

Where Q is heat of diffusion or solution.

N is Avogadro's number

h is Planck's constant

R is the gas constant

T is the absolute temperature

e = 2.718 +

S is the interatomic distance.

It has been observed that D varies to some extent as concentration of solute (c) varies, and this is not indicated by equation (4).

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From equation (4) it is apparent that the diffusion coefficient is much larger at higher temperatures, and also that its value depends on the properties of the solute material (in the steel). Equation (4) does not indicate the effect which the presence of one or more alloying elements would have on the diffusion coefficient of carbon. in iron.

From consideration of equations (3) and (4) it is observed that rate of carburization, as measured by mass of carbon diffused into the metal, is greater if the carbon gradient (dc/dx), the diffusion coefficient (D), or the absolute temperature (T), is greater.

Furthermore, a greater carbon concentration at the interface will produce a greater depth of case; a large diffusion coefficient will produce a greater depth of case, other conditions being equal.

Mehl /22/ has presented a review of the subject of diffusion in solid metals. It may be said that the theory thus presented has great potential value for analysis of carburization processes. Unfortunately most of the research in carburization yields too little information to permit computation of diffusion coefficients, and thus fails to contribute to knowledge of diffusion. In particular, evaluation of the quantity "$\frac{dm}{dt}$" equation (3) would be most useful. The total mass of carbon diffused (the area under the depth-concentration curve) gives a means of estimating relative magnitude of mass "m". (equation 3).

Additional data is needed if the true value of "$\frac{dm}{dt}$" is to be computed.

No information is available on the effect of the structure of a given alloy on the rate of carburization which may be attained. At the carburizing temperature the steel is austenitic and the effects of previous treatment are not apparent in the structure. However,

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there are properties of the steel associated with the McQuaid-Ehn grain size /2//3//20//23/ which are retained after heating and cooling steel through the austenitic range. In spite of the work of Grossman /2//3/ and others the true cause of the inherent grain size of the steel is not definitely known. It is at least possible that the previous treatment of the steel may have some effect on its rate of carburization.

PROPERTIES OF THE MATERIAL UNDER TEST

Two steels of an alloy content approximating that of Krupp armor steels, and two steels of somewhat lower alloy content were selected for test. Analyses of these steels are given in Table I. They were selected from several regular lots offered by commercial concerns, the idea being to conduct the tests on samples representative of good commercial practice.

These steels are characterized by very high strength, good ductility, toughness, and resistance to shock; and are sluggish in response to heat treatment, becoming pearlitic only when annealed slowly. Steels of Krupp analysis are known to be susceptible to temper brittleness under some donditions of heat treatment.

Steel SAE No. 1020 is a plain carbon steel included in the investigation as a control.

The material was furnished by the respective manufacturers in rods approximately 1" in diameter. Steels A and B being hot rolled and steels C, D and E being hot forged. The samples were examined for elongated grains which would indicate too low finishing temperature. None were found.

Table III gives the data on critical points of these steels,

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the values given in the literature /21/ for the nominal composition being correctedfor variations from this composition by use of factors determined by Reed /18/. In no case did the value of this correction exceed 3°F. The values of carbon content of the eutectoid are also based on work of Reed./18/.

This work of Reed, while not very accurate, is the best that is available for the purpose.

EXPERIMENTAL PROCEDURE

In order to determine the effect of initial structure of the sample on rate of diffusion, samples of each steel were heated to various temperatures, for various times, as indicated in Table II.

Various means were used to protect the specimens from oxidation in the cases of Steels A and B, Steels C and D, and E, were treated in a chromium steel container in a nitrogen atmosphere. A Westinghouse Globar furnace was used, with automatic temperature control, and a separate thermocouple was used to check temperatures as close to the specimens as possible.

Each specimen was centered in a lathe, and turned accurately to a cylinder. In so doing, a layer of metal from 1/16" to 1/8" thick was cut off from the surface, thus disposing of material which might have undergone decarburizing during heat treatment. A feed of 0.005" per revolution was used on the final cut to give uniform surface

The specimens were then carburized in batches as indicated in Table II, in a mixture of 60% powdered charcoal by weight, and 40% powdered barium carbonate. It should be noted at the temperatures used the samples were initially above the upper critical point (Ac3) and hence austenitic. The original grains were recrystallized.

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This work of [illegible] is available for the [illegible].

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The specimens were then carburized in tubes as indicated in Table II, in a mixture of 60% powdered charcoal by weight, and 40% powdered barium carbonate. It should be noted at the temperatures used the samples were initially above the upper critical point (Ac_3) and hence austenitic. The original grains were recrystallized.

Every sample was carburized 12 hours at the temperature indicated in Table II; this time does not include time to raise the specimen to temperature or cool it. The cooling rates varied in a regular manner from 2°F. per minute shortly after the current was turned off to 1°F. per minute at about 300°F.; and from 300°F. to room temperature cooling, rates were below 1°F. per minute.

After cleaning, the specimens were returned to the lathe and successive layers of metal 0.0070" to 0.0150" thick were removed and the turnings analyzed for carbon content by the combustion method, Careful records were kept of the diameters of the specimens after each operation in order that the location of each sample of metal analyzed might be used in plotting curves of carbon concentration against depth. A sufficient length was left on each specimen so that a sample 1" from the end of the speciman could be removed for microscopic examination. Photomicrographs which appear to be of interest are included in this report.

Conclusions in regard to rates of carburization were based on examination of depth-carbon concentration curves. This technique gives more accurate measure of depth of case than visual examination of microstructures and also reveals the distribution of carbon within the case.

The relative mass of carbon diffused, as given by the tables, may be converted to lb. of carbon per square inch of area per hour by multiplying by 5.9 x 10 - 13.

In making up the tables, the area under the depth-carbon concentration curve was measured down to the 0.25% carbon ordinate in the case of Steel A and down to the 0.40% carbon ordinate in the case of Steels B, C, D, and E. These values correspond to the approximate carbon contents of the original samples. The purpose of

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this procedure was to omit from the calculations the original carbon contents, and base conclusions on the mass of carbon added in each case.

Furthermore, errors due to minor variations in initial carbon content are thus reduced to negligible proportions. ~~Steel~~ The initial diffusion rate is higher due to higher carbon gradient. (Equation 3.) The error due to low initial carbon content of steel A is "on the side of safety". No matter what its numerical value, it can not affect the verity of the conclusion to be stated.

RESULTS

Effect of initial structure on rate of carburization.

Table II and figure 11 show that rate of carburization in Steel C is practically independent of initial grain size as produced by annealing. Steel C has a slightly lower alloy content than the usual Krupp analysis of armor steel. Rate of carburization is very slightly increased by long heating just below the critical range, so that the sample is partly spheroidized. (Specimen C 4).

The rate of carburization of Steel D is increased to a marked degree by increasing initial grain size by annealing, as may be noted by reference to Table II and figures 11 and 14. The rate of carburization is also increased by spheroidizing treatment. (Specimen D 4).

The rate of carburization of Steel E is practically independent of initial heat treatment. (Table II figure 11).

The rate of carburization of Steel A, which is a plain carbon steel, is increased somewhat by annealing to increase grain size (Table II and figures 12 and 15). A somewhat greater increase in rate of carburization was obtained by a quenching treatment. (Specimens A 5 and A 6).

In Steel B, which has an alloy content slightly greater than the usual Krupp analysis for armor steel, the effect of initial structure was in part obscured by the variety of heat treatments undertaken. A coarse-grained structure obtained by air cooling (martensitic) permitted a lower rate of carburization than a structure obtained by annealing. (Table II and figures 12 and 16).

The average mass of carbon diffused is computed in each case where a number of samples had received identical treatment, and the

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The rate of carburization of steel D is increased to a marked degree by increasing initial grain size by annealing, as may be noted by reference to table II and figures 13 and 14. The rate of carburization is also increased by spheroidizing treatment. (Specimen D 4).

The rate of carburization of steel B is practically independent of initial heat treatment. (Table II figure 11).

The rate of carburization of steel A, which is a plain carbon steel, is increased considerably by annealing to increase grain size (Table II and figures 12 and 15). A somewhat greater increase in rate of carburization was obtained by a quenching treatment. (Specimens A 6 and A 8).

In steel E, which has an alloy content slightly greater than the usual Krupp analysis for armor steel, the effect of initial structure was in part obscured by the variety of heat treatments undertaken. A coarse-grained structure obtained by air cooling (martensitic) permitted a lower rate of carburization than a structure obtained by annealing. (Table II and figures 12 and 16).

The average mass of carbon diffused is computed in each case where a number of samples had received identical treatment, and the

results tabulated in the last four lines of Table IV.

Effect of alloy content on rate of carburization. (Figures 11 and 12).

In analyzing the effect of alloy content on rate of carburization, it is necessary to make allowance for the effect of initial grain size. If the results for all samples of each steel are considered, as averaged in Table IV, Steel A has the lowest rate of carburization, C and E carburize at the same rate, and Steel D has the highest rate. Steel B was carburized at a lower temperature, and the rate of carburization was low. No definite conclusion can be drawn by comparing this rate with rates of carburization of the other steels. If the carburizing rates of the steels in the fine-grained condition are compared, (Table II), it will be observed that Steel D carburizes at the same rate as steels C and E, Steel A still showing the lowest rate of carburization.

Carbon, chromium, molybdenum, and to a less degree manganese, may be lost from the surface of the specimen in heat treating.

Examinations of the microstructure indicated that the layer of metal removed after heat treating was in each case sufficient to assure that the sample as carburized was homogeneous and the original alloy content unaltered, except in samples A4, B3, B4 and B5. As the layer removed from Sample E1 was comparatively thin, a chromium analysis was made of the outer layer removed after carburization, in addition to the carbon analysis. Chromium content was 0.71% as compared with an original chromium content of 0.75%. From this it was concluded that the original alloy content was not changed sufficiently to affect the results. Specimen A4 was almost completely

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Examinations of the photomicrographs indicated that the layer of metal removed after heat treatment is in each case sufficient to assure that the sample [illegible] carburized was homogeneous and the original alloy content unaltered, except in samples A, [illegible], [illegible] and [illegible]. As the layer removed from sample A1 was comparatively thin, a chromium analysis was made of the outer layer removed after carburization, in addition to the carbon analysis. Chromium content was 0.7[illegible] as compared with an original chromium content of 0.75%. From this it was concluded that the original alloy content was not changed sufficiently to affect the results. Specimen A4 was almost completely

decarburized before carburizing. (Table II). The rate of carburization was 20% less than in a sample which had received a similar heat treatment and which had been protected from decarburization. This result is consistent with the findings of Bramley /26/.

Notes on microstructure.

The grain size of both the case and the core of Steels A and D after carburizing was influenced by the initial grain size, initially coarse-grained samples showing larger grains after carburizing in both the case and the core. (Figures 3, 4, 7). These steels were carburized less than 200° F. above the upper critical (Ac3) point. The final grain size of Steels C and E carburized more than 200° F. above the Ac3 point was independent of the initial grain size.

The depth of carburization as determined by microscopic examination of the etched specimens at 10x and 100x was consistent with the determinations based on carbon analysis in the cases of Steels A and B, and was inaccurate in the cases of Steels C and D. The observed depth of case is sensitive to minor changes in technique in etching with 4% nitric acid in alcohol.

The determination of grain size by comparing with standard grain size charts and converting grain size number to linear dimension of the grain by computation was found the most satisfactory method, in view of the variation in the microstructures of the different steels. In the spheroidized steels, for example, it would be difficult to devise a grain count method that would describe the appearance of the steel.

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heat treatment [illegible] had been [illegible] carburization.
This result [illegible]

Notes on microstructure.

The grain size [illegible]
D after carburizing [illegible] grain size, initi-
ally coarse-grained [illegible] carburizing
in both the [illegible]
were [illegible] less than [illegible] critical [illegible]
point. The [illegible] grain size [illegible] more than
200° F. above the [illegible] point [illegible] in
size.

The depth of carburization as determined by microscopic exami-
nation of the etched [illegible] with
the determinations based on carbon analysis in the cases of steels
A and B, and was inaccurate in the cases of steels C and [illegible]. The ob-
served depth of case is sensitive to minor changes in technique in
etching with [illegible] nitric acid in alcohol.

The determination of grain size by comparing with standard
grain size charts and converting grain size number to linear dim-
ension of the grain or computation was found the most satisfactory
method, in view of the variation in the microstructures of the
different steels. In the spheroidized steels, for example, it
would be difficult to devise a grain count method that would describe
the appearance of the steel.

Samples of Steels C and D before carburizing were examined under a microscope 2000x. In the fine-grained samples of Steel D the grain boundary constituents (etched dark with the nital) seemed to form networks about the light-colored grains; whereas in the other samples examined the grain boundary constituents were more discontinuous. In spheroidized samples, of course, nothing resembling grain boundary networks were observed.

DISCUSSION

Effect of initial structure of steel on rate of carburization

In this work no exceptions were found to the statement that initial grain size affected the final grain size and rate of diffusion of carbon, when the carburizing temperature was less than 200°F. above the upper critical point (Ac3).

Nothing has been said of the austenitic grain size of the steels which were carburized. It is not believed that variations in austenitic grain size or discontinuities in the lattice structure of the metal affect the rate of carburization. Mehl, in commenting on the work of Mooradian and Norton /7/, observed that the diffusion in some binary metallic systems occurs at a rate apparently independent of the presence of grain boundaries, and recently referred to the fact that this applies as well to the iron-carbon system /22/. It should be said that the experimental evidence rests on a limited number of observations, and there is at least one exception; thorium diffuses in tungsten much more rapidly along the grain boundaries than through the grains /8/.

However, Epstein and Rawdon /14/ observed that abnormal steels carburized at a lower rate than normal steels, the latter of course having a much larger initial grain size. Apparently they did not investigate the effect on rate of carburization of varying the grain size of one lot of steel. Rowland and Upthegrove/5/ recently determined that large initial grain size of steel accelerated the loss of carbon through surface decarburization.

An explanation of the variations in rates of diffusion described above, may be stated as follows:

DISCUSSION

Effect of initial structure of steel on rate of carburization.

In this work no exceptions were found to the statement that initial grain size affected the final grain size and rate of diffusion of carbon, when the carburizing temperature was less than 200°F. above the lower critical point (Ac1).

Nothing has been said of the austenitic grain size of the steels which were carburized. It is not believed that variations in austenitic grain size or distortion in the lattice structure of the metal affect the rate of carburization. Mehl, in commenting on the work of Hocrwitz and Horton /7/, observed that the diffusion in some binary metallic systems occurs at a rate apparently independent of the presence of grain boundaries, and recently referred to the fact that this applies as well to the iron-carbon system /12/. It should be said that the experimental evidence rests on a limited number of observations, and there is at least one exception; thorium diffuses in tungsten much more rapidly along the grain boundaries than through the grains /8/.

However, Hostetter and Rawdon /14/ observed that abnormal steels carburized at a lower rate than normal steels, the latter of course having a much larger initial grain size. Apparently they did not investigate the effect on rate of carburization of varying the grain size of one lot of steel. Rowland and Upthegrove/5/ recently determined that large initial grain size of steel accelerated the loss of carbon through surface decarburization.

An explanation of the variations in rates of diffusion described above, may be stated as follows:

Rate of diffusion of carbon in the austenitic grains of the alloy is more rapid than the rate of diffusion in the material at the grain boundaries. These "grain boundary constituents" are so stable that they remain effective as barriers to the diffusion of carbon about 200°F., above the critical point (Ac3).

Of course, if the material is spheroidized, it is reasonable to expect that the "barriers" will be broken up and the resistance to diffusion diminished. A statement of the composition of these "grain boundary constituents" is not absolutely necessary.

McQuaide states /23/ that inherent grain size (as evidenced by the McQuaid-Ehn grain size for instance) depends on the presence of compounds of aluminum, vanadium, etc., at grain boundaries /4/. Davey /9/ believed that carbides, nitrides, and oxides segregated in the dendritic structure of steel impede the diffusion of carbon. It will no doubt occur to the reader that the same constituents (or properties) which influence the McQuaid-Ehn grain size may possibly affect the rate of diffusion of carbon. However, there is only indirect evidence at best to support conclusions in regard to the effect of non-metallic inclusions on the structure of steels.

EFFECT OF VARYING ALLOY CONTENT OF STEEL ON RATE OF CARBURIZATION

The work of Houdremont and Schrader /13/ has been referred to. As a result of this work they listed certain elements which when added to steel in amounts up to 6% accelerated diffusion; others which retarded diffusion; and still others which had little effect on diffusion. The effect of each alloying element on final grain size was also recorded. The writer plotted the case depths against final grain sizes as obtained by Houdremont and Schrader, and observed

Rate of diffusion of carbon in the [illegible] of the alloy is more rapid than [illegible] diffusion [illegible] the grain boundaries. [illegible] stable [illegible] they remain effective barriers [illegible] carbon about [illegible] the critical point [illegible].

Of course, if [illegible] it is reasonable to expect that the "barriers" will be [illegible] diffusion [illegible]. A statement of the composition of these "grain boundary constituents" is not absolutely necessary.

McQuaid states /7/ that the inherent grain size (as evidenced by the McQuaid-Ehn grain size for instance) [illegible] presence of compounds of aluminum, vanadium, etc., [illegible] /9/. Davey /8/ believed that carbides, nitrides, and oxides [illegible] in the dendritic structure of steel [illegible] carbon. It will no doubt occur to the reader that the same constituents (or properties) which influence the [illegible] grain size may possibly affect the rate of diffusion of carbon. However, there is only indirect evidence at hand to support such conclusion in regard to the effect of non-metallic inclusions on the structure of steels.

EFFECT OF [illegible] ALLOY CONTENT OF STEEL ON RATE OF CARBURIZATION

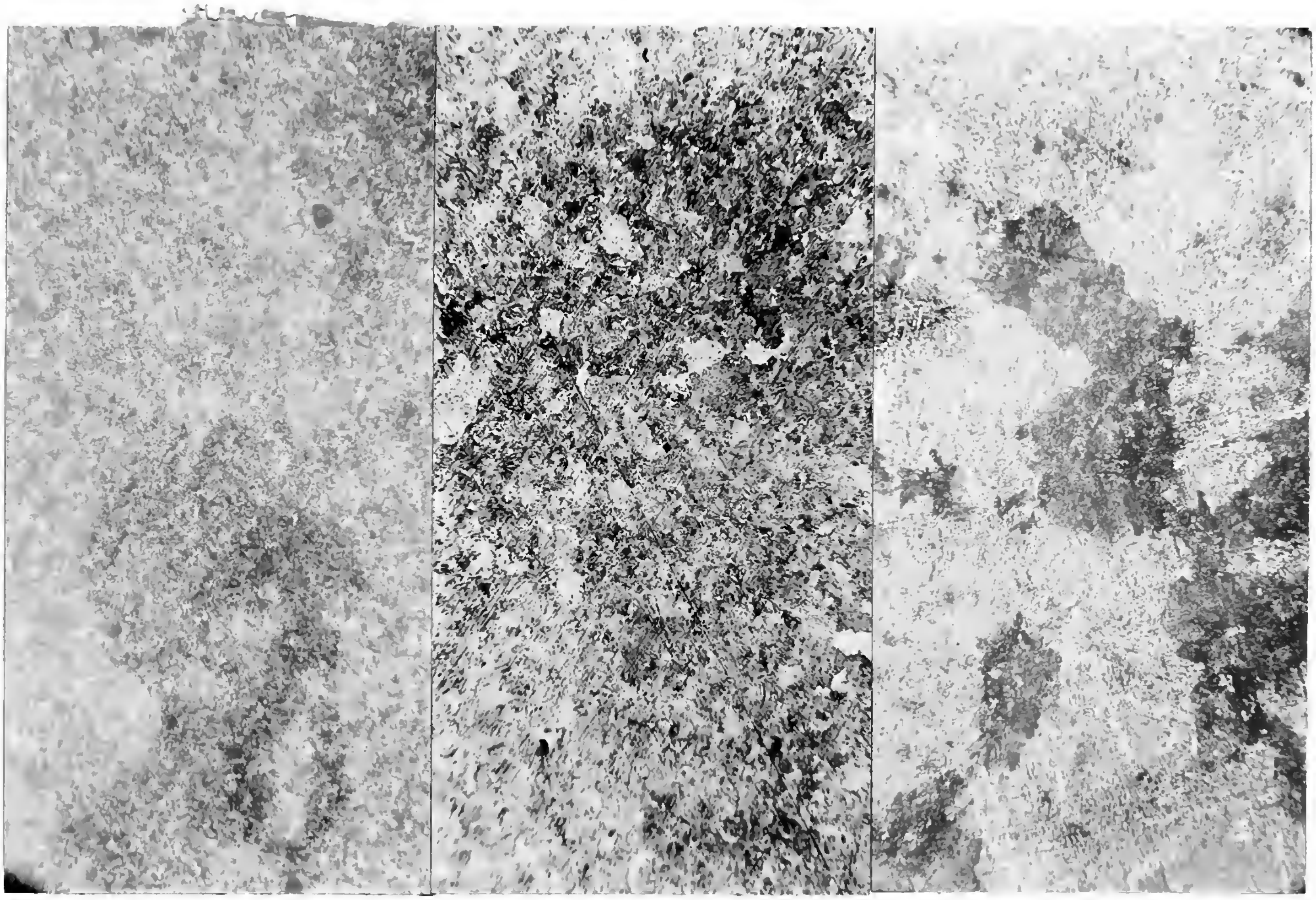
The work of Houdremont and Schrader /13/ has been referred to. As a result of this work they listed certain elements which when added to steel in amounts up to 5% accelerated diffusion; others which retarded diffusion; and still others which had little effect on diffusion. The effect of each alloying element on final grain size was also recorded. The writer plotted the case depth against final grain sizes as obtained by Houdremont and Schrader, and observed

that rate of diffusion increased in a fairly regular manner as the grain size of the carburized specimens increased. In most cases it did not seem to matter greatly which alloying element was present. Aluminum and chromium were conspicuous exceptions. Each one decreased the rate of diffusion and increased the grain size. The information available was insufficient to attempt a correlation of rate of diffusion with initial grain size.

In the opinion of the writer, a more complete understanding of the effect of alloying additions on rate of diffusion would result if these additions were studied from the point of view of their effect on the grain size of the steel.

ACKNOWLEDGEMENT

The writer desires to express his appreciation of the cooperation of the Allegheny Steel Company, the Carnegie-Illinois Steel Corporation, the Inspector of Naval Material at Munhall, Penna., the Republic Steel Corporation, and the Midvale Company, in furnishing samples required for test, and performing chemical analyses; and of the personnel of the Metals Research Laboratory and Department of Metallurgy, Carnegie Institute of Technology, for valuable advice and suggestions.



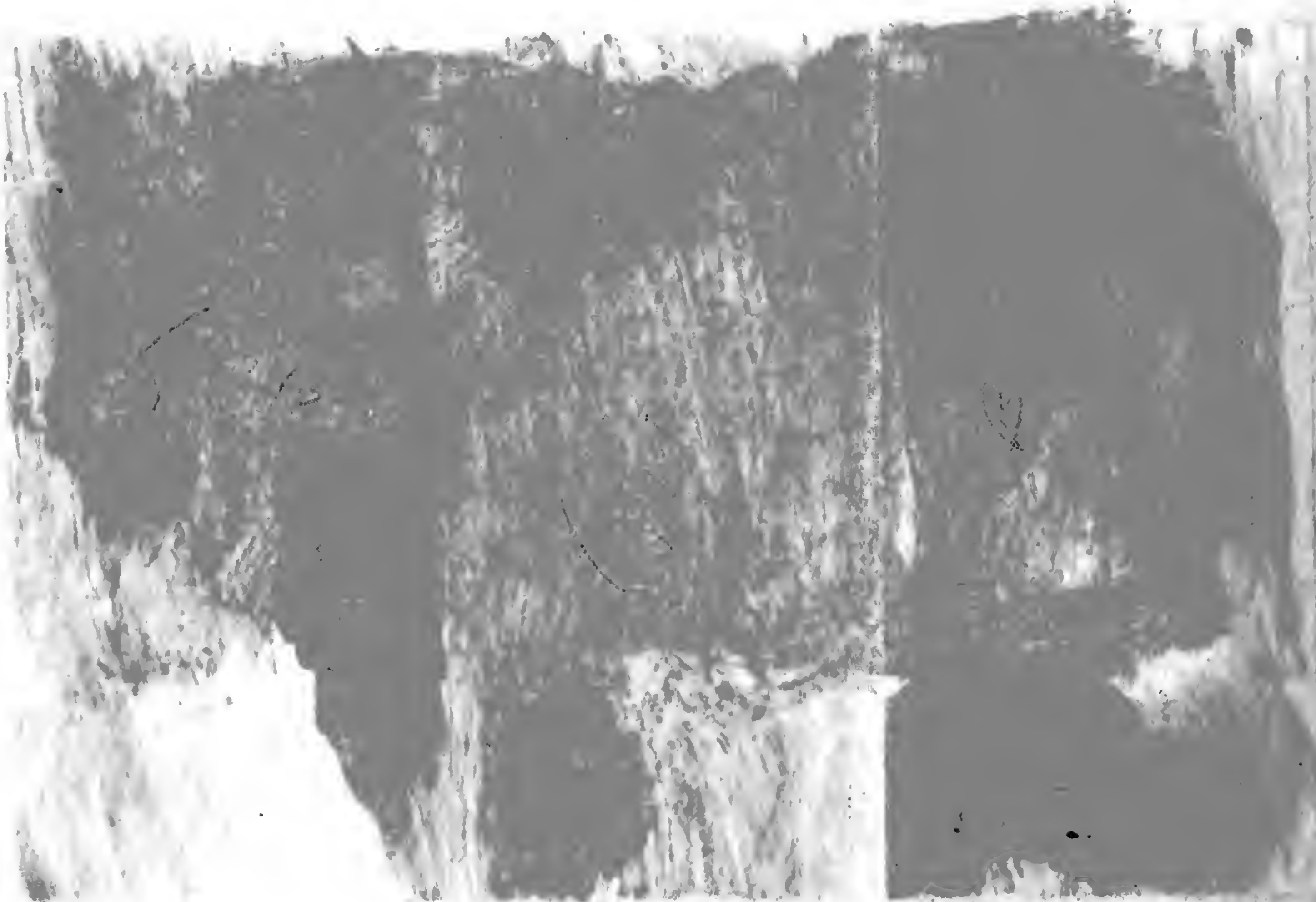
a
Annealed from 1600
Steel C

b
Annealed from 1850

c
Annealed from 2100F

Figure 1.

Magnification 100 X



a
Annealed from 1600
Steel C

a At 1600 — b At 1850 — c At 2100° F.

At 1600

Annealed prior to carburizing at temperatures indicated. Carburized at 1615° F. for 12 hours. Steel C.

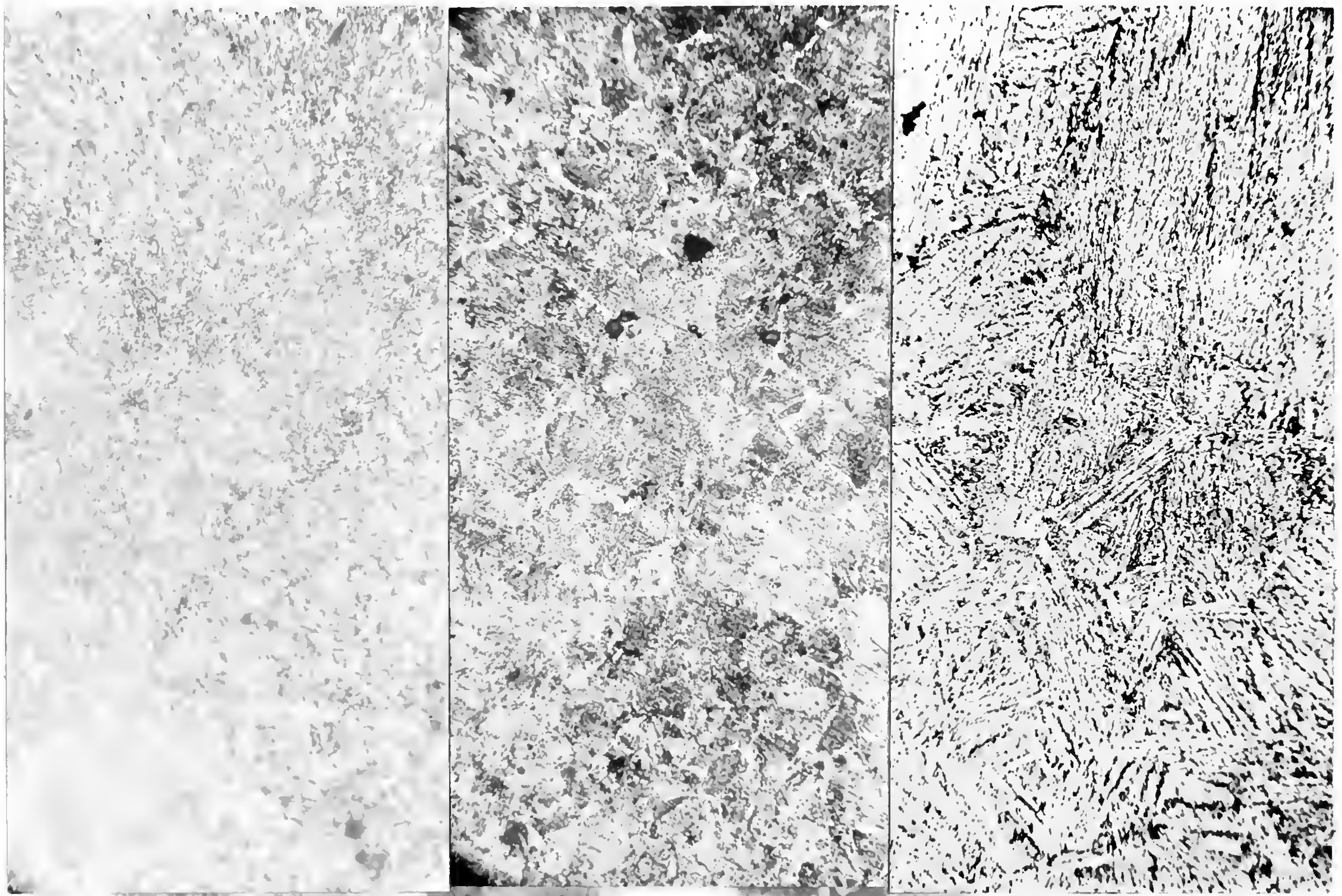
Figure 2.

Magnification 100X

a At 1600 — b At 1850 — c At 2100° F.

Annealed prior to carburizing at temperatures indicated. Carburized at 1615° F. for 12 hours. Steel 2.

Figure 4.

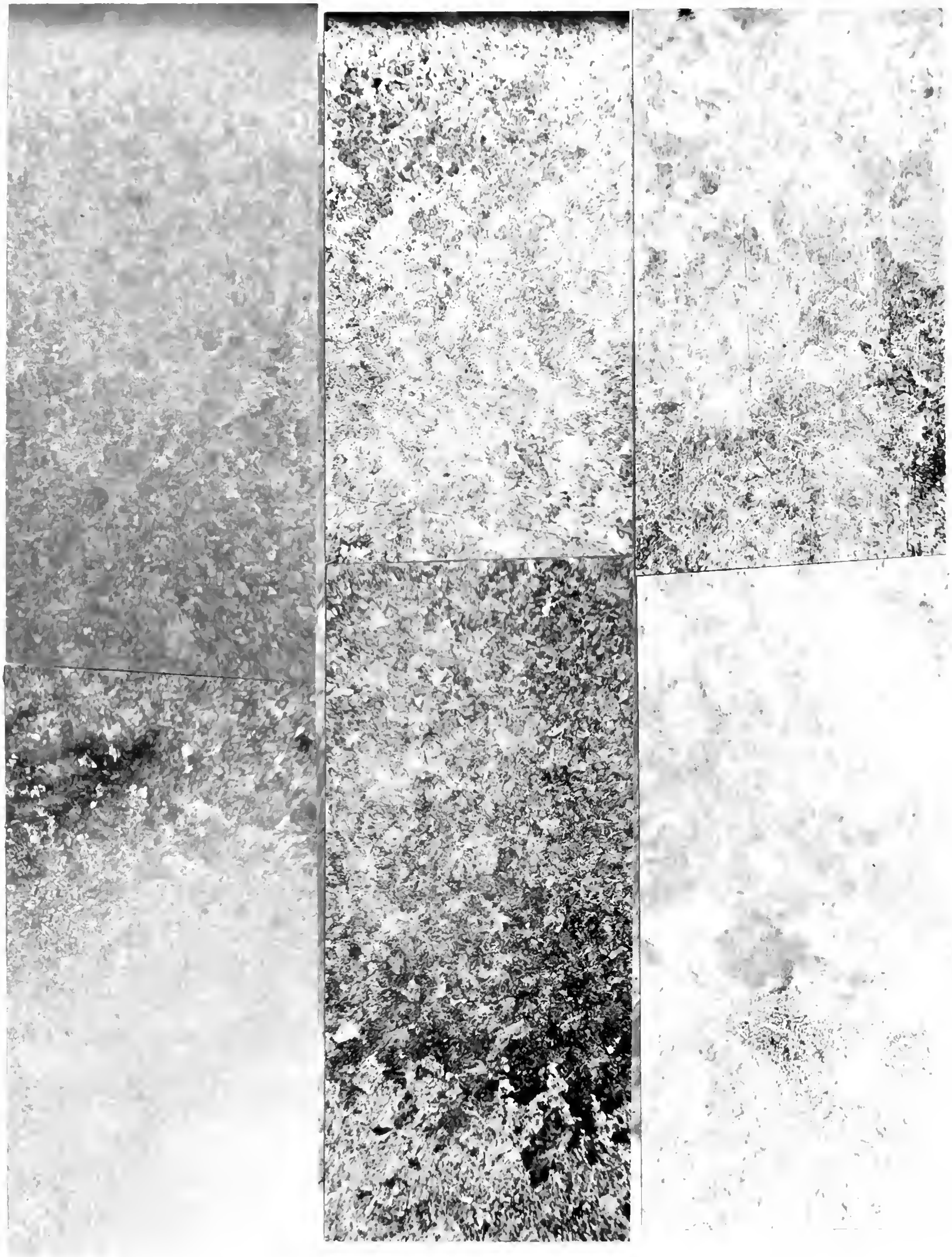


a Annealed from 1600 | b Annealed from 1850 | c Annealed from 2100° F.

Steel D

Figure 3.

Magnification 100 X



a Annealed from 1600 b Annealed from 1850 c Annealed from 2100° F.

Heat treatment prior to carburizing as indicated. Carburized at 1615° F.

Steel D.

Figure 4..

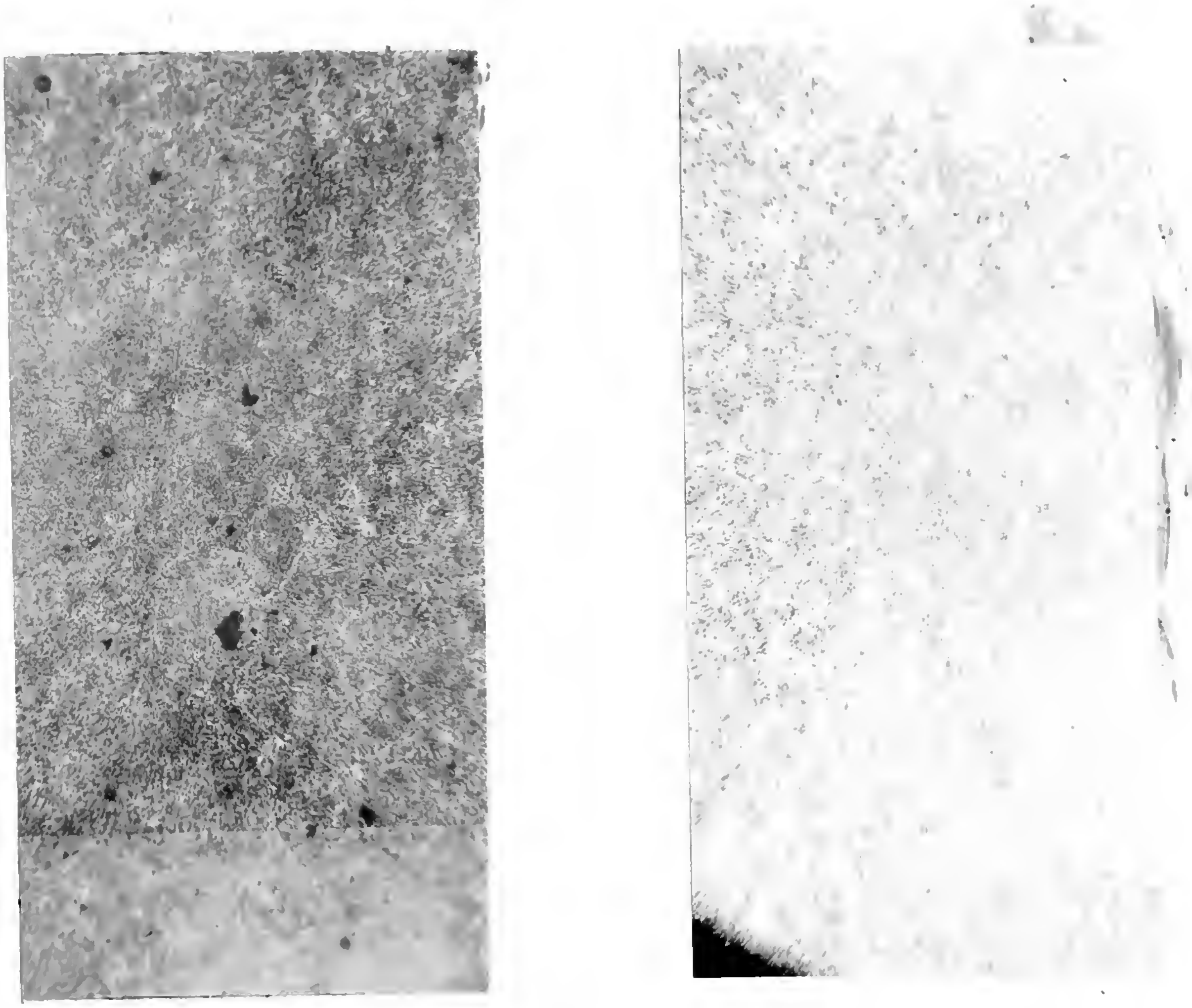
Magnification 100 X

a — Annealed from 1600 b — Annealed from 1850 c — Annealed from 2100° F.

Heat treatment prior to carburizing as indicated. Carburized at 1650° F.
Steel D.

Figure 4.

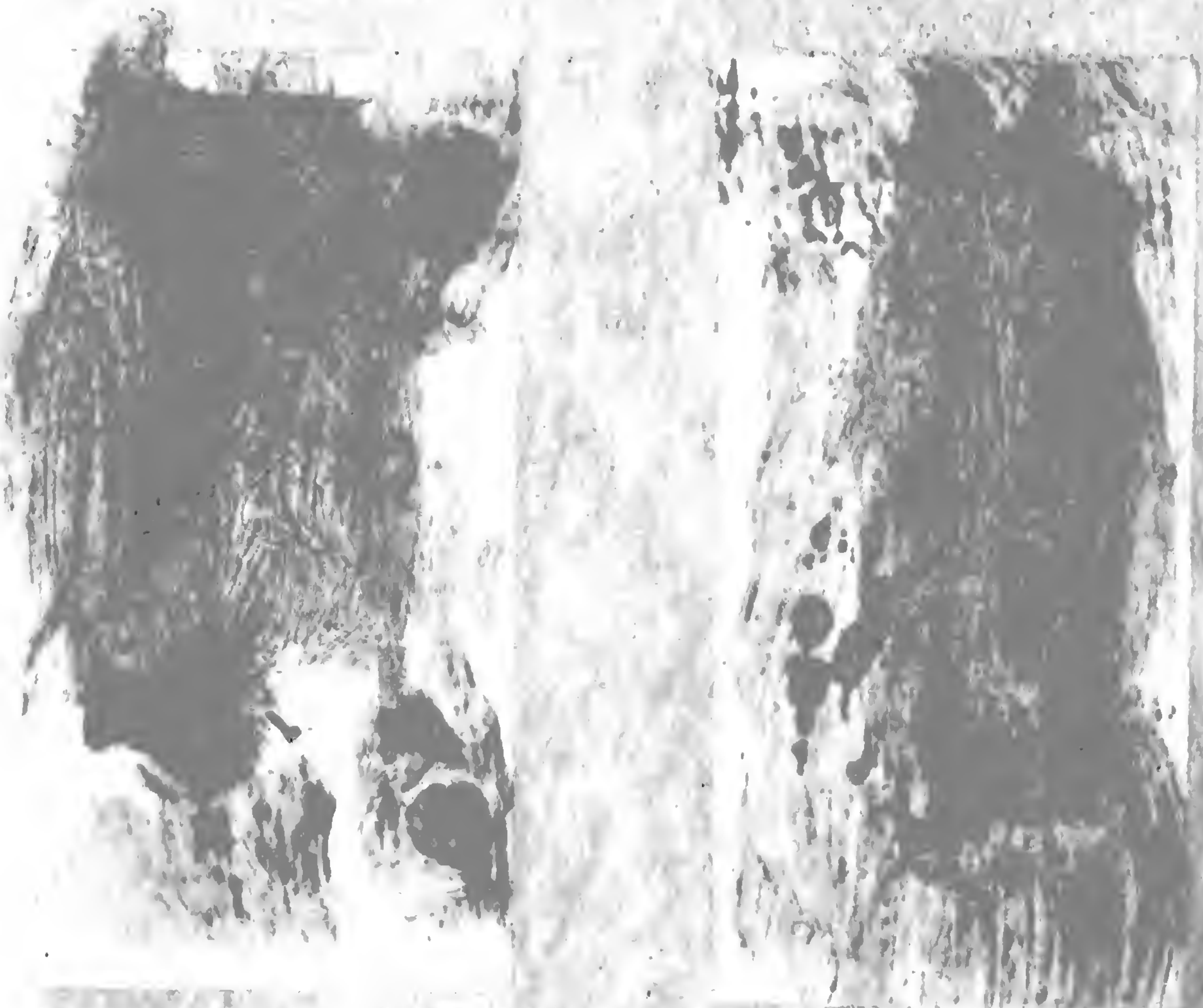
Magnification 100 X



C 4 D 4

Figure 5..

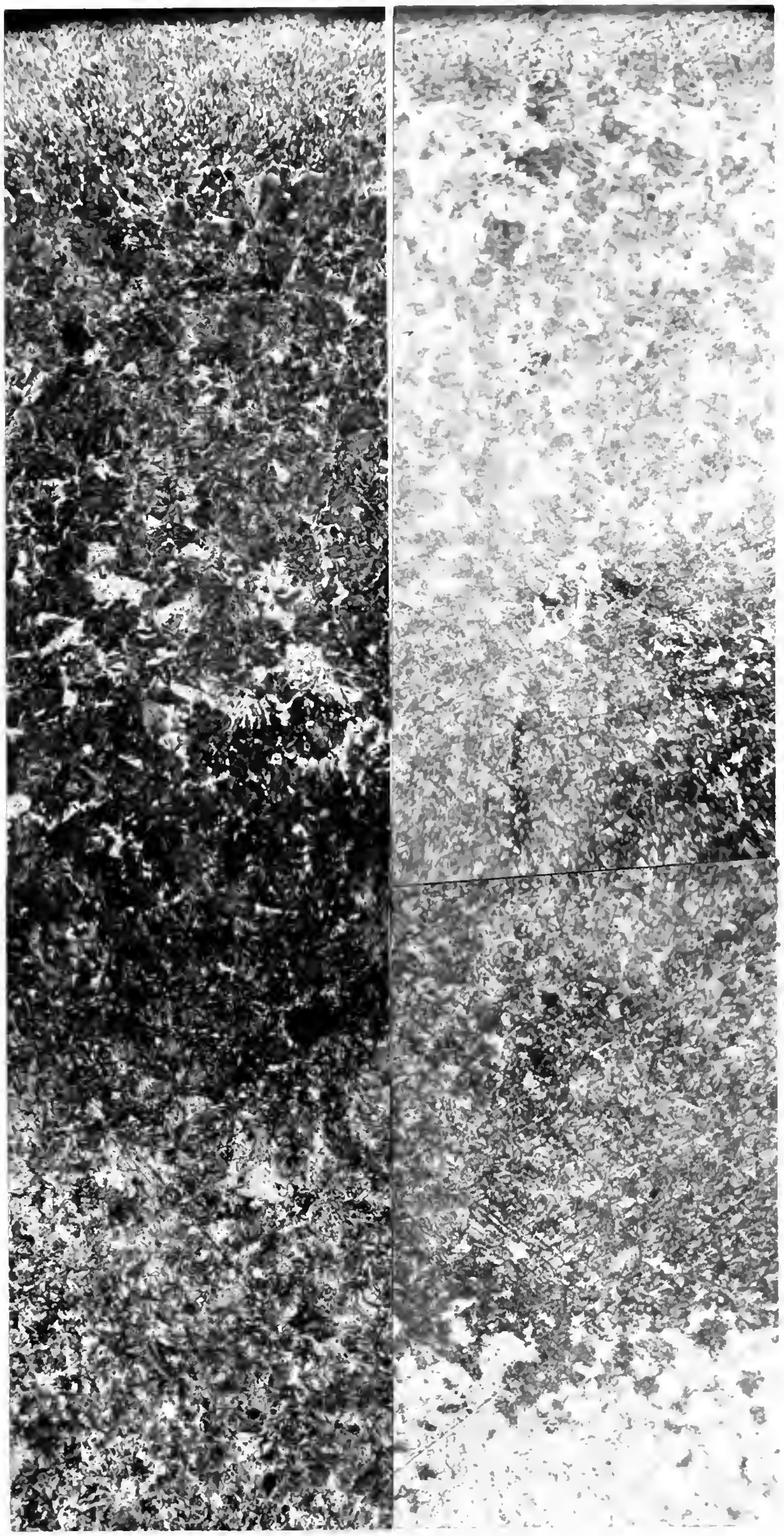
Magnification 100 X



C 4 D 4

Figure 5..

Magnification 100 X



a b

Steel C Steel D

Annealed prior to carburizing at 1300 F. ~~for~~ Carburized at 1615 for 12 hrs

Figure

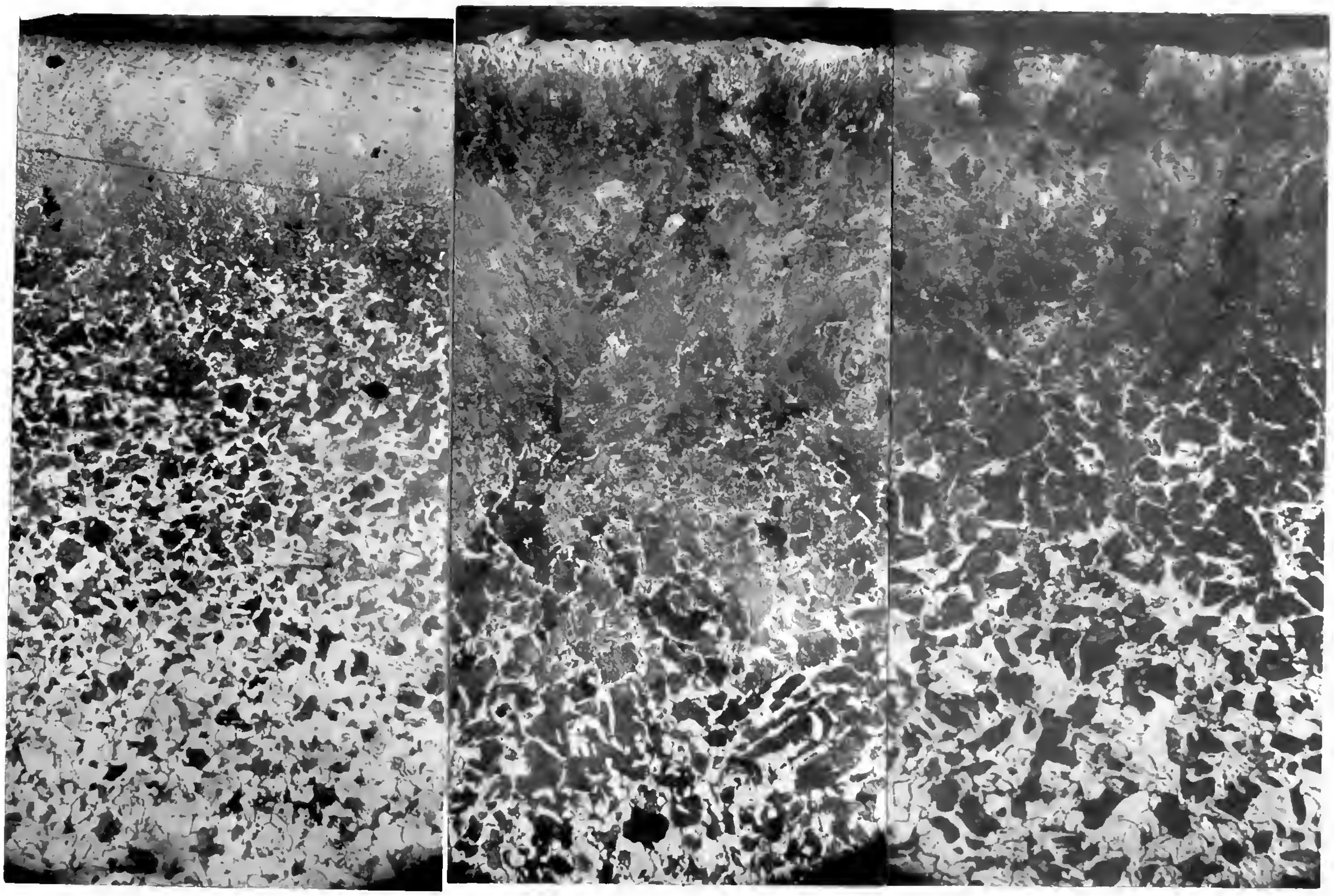
Magnification 100X

Steel D Steel C

[illegible]

[illegible]

Magnification 100X



a
Annealed from 1800 F

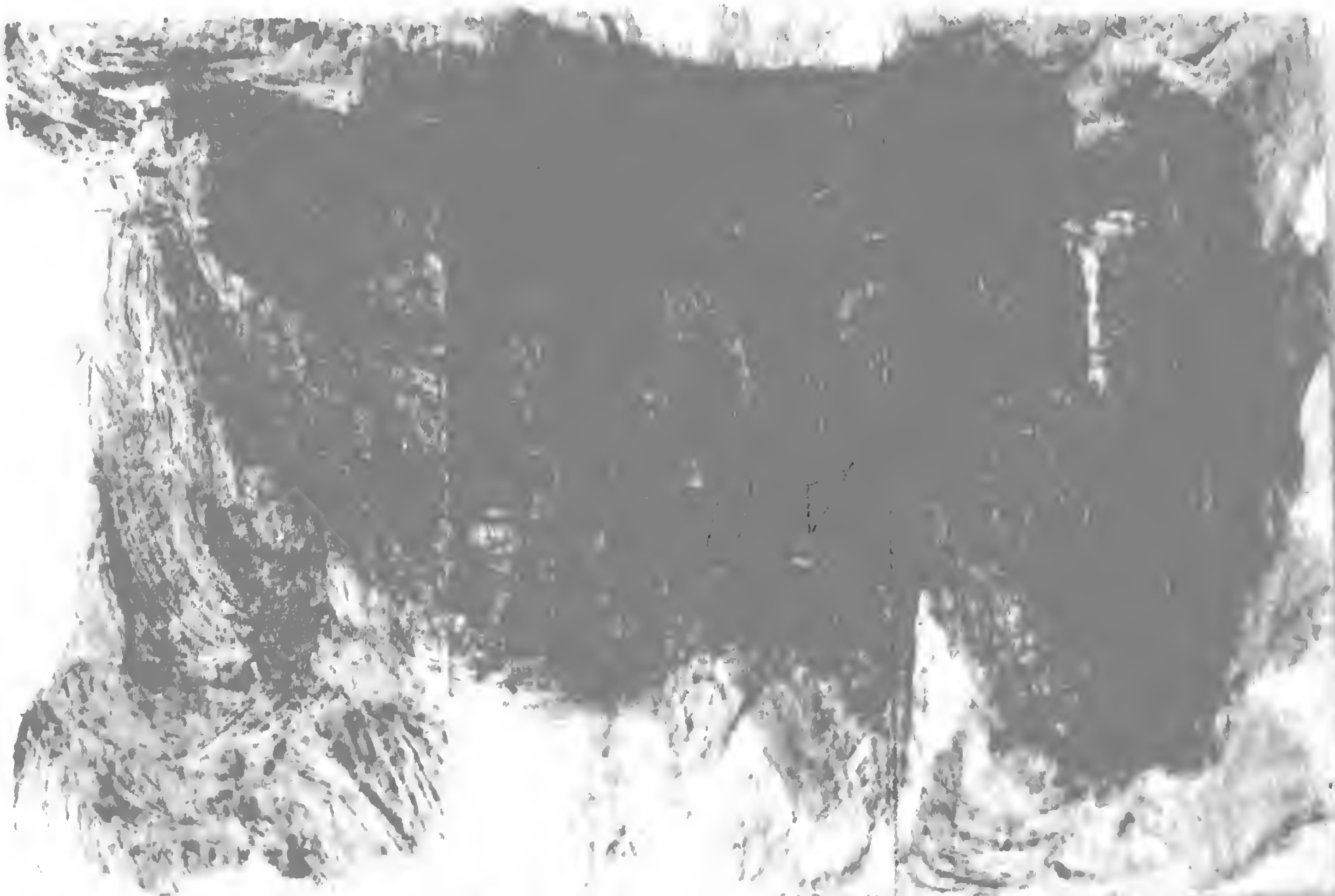
b
Annealed from 2100 F

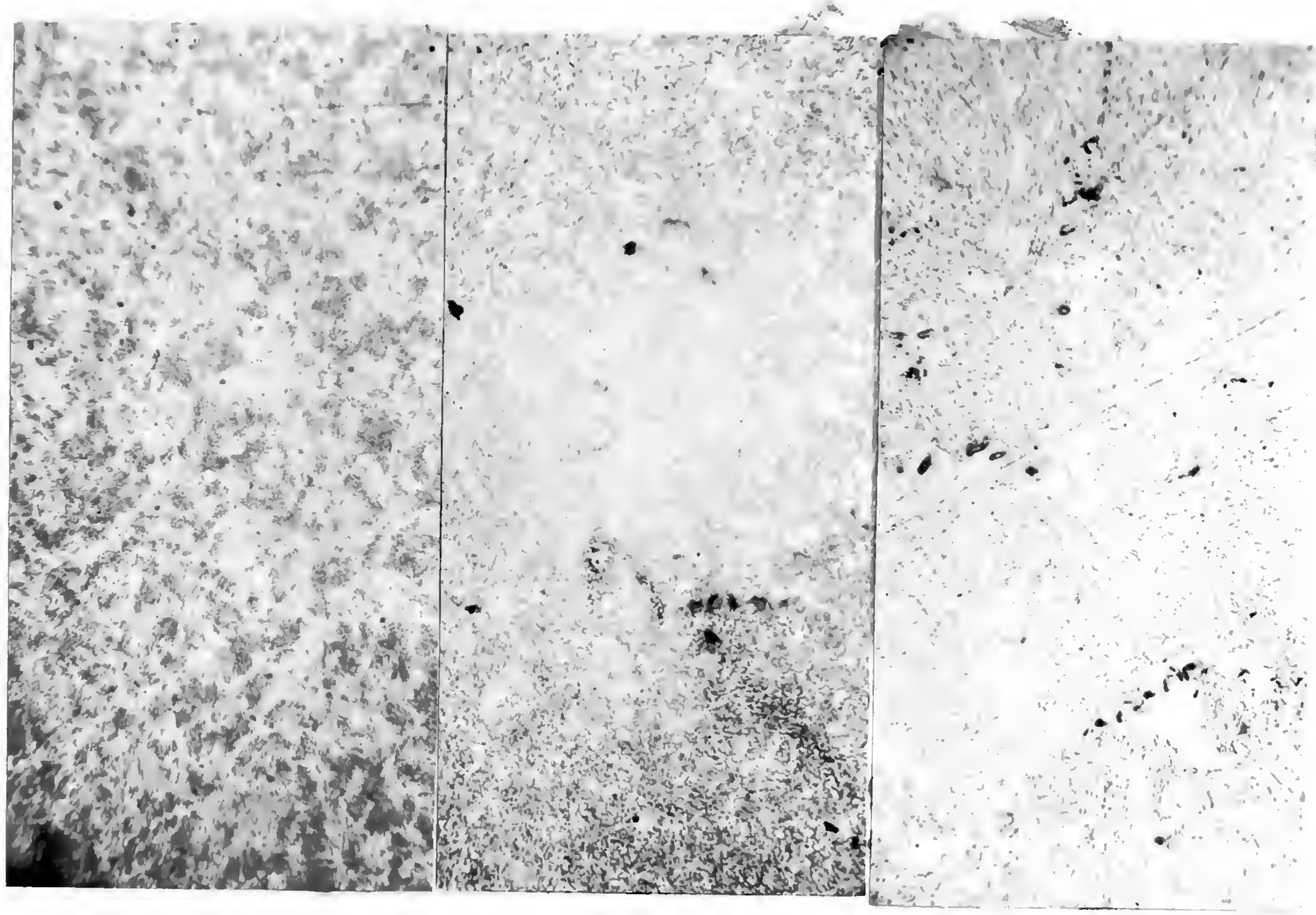
c
Annealed from 2100 F
Heavily decarburized in heat treating.

Treatment prior to carburizing as indicated. Carburized at 1635 F for 12 hours. Steel A.

Figure 7.

Magnification 100 X





a
B 1

(Boo)

b
B 2

(B4 or 6)

c
B 3

B 12

Figure 8

Magnification 100 X

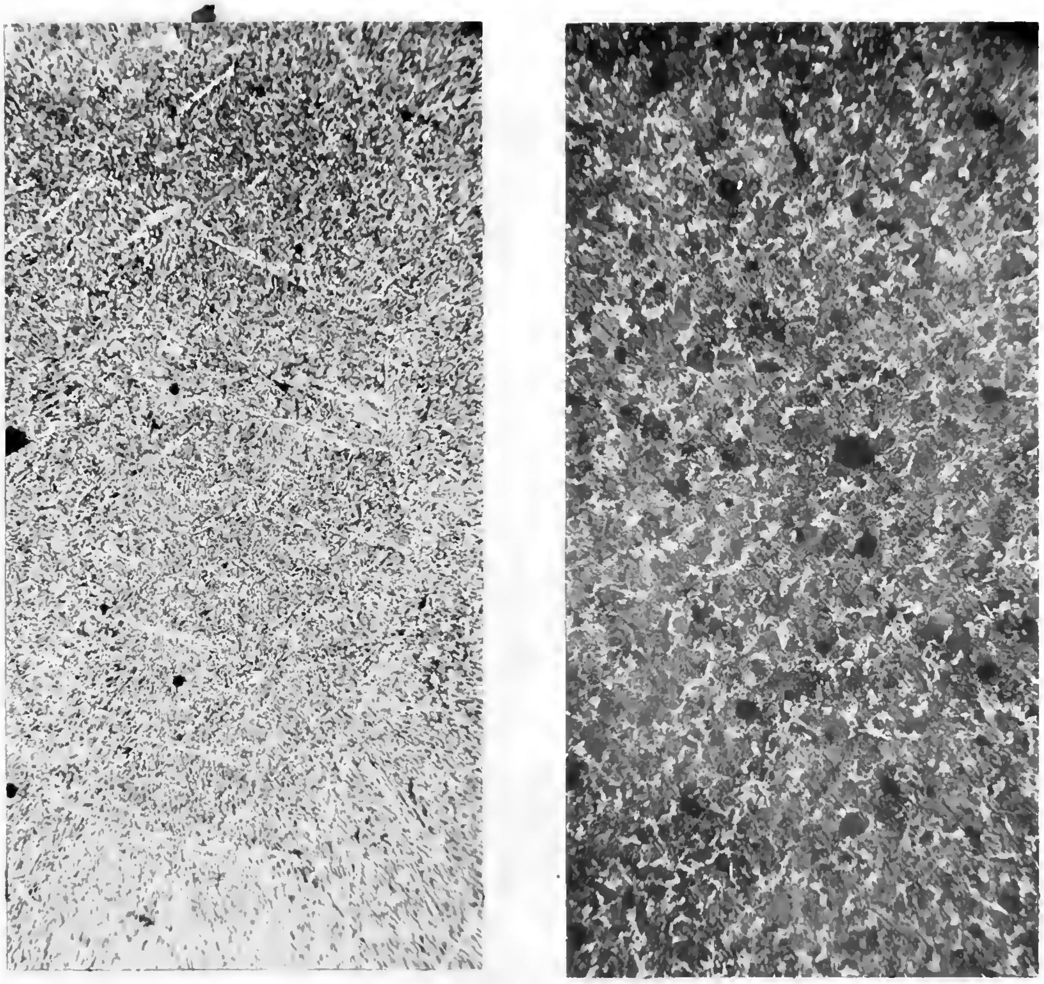
a
P 1
(Boo)

b
P 2
(P4 or 6)

c
P 3
P 12

Figure 8

Magnification 100 X

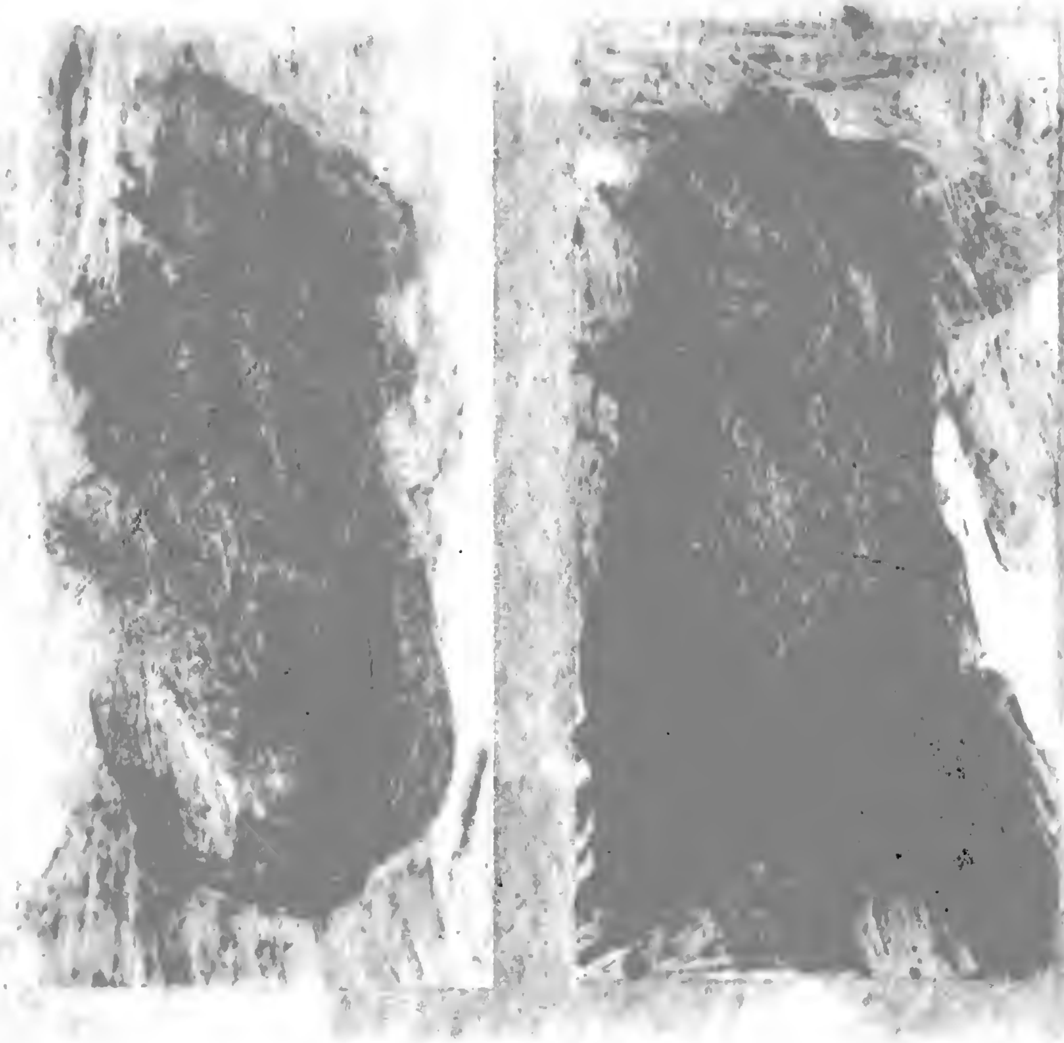


a
B4
(B7)

b
E1

Figure 9

Magnification 100 X

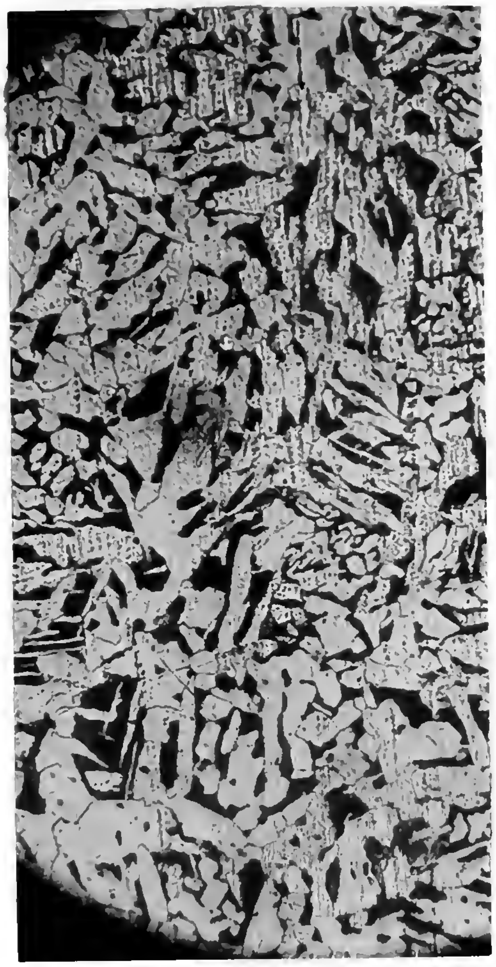


a
F4

b
F1

Figure 9

Magnification 100 X



Steel A
Annealed at 2100° F.
Figure 10

Steel A
Annealed at 2100° F.
Figure 10

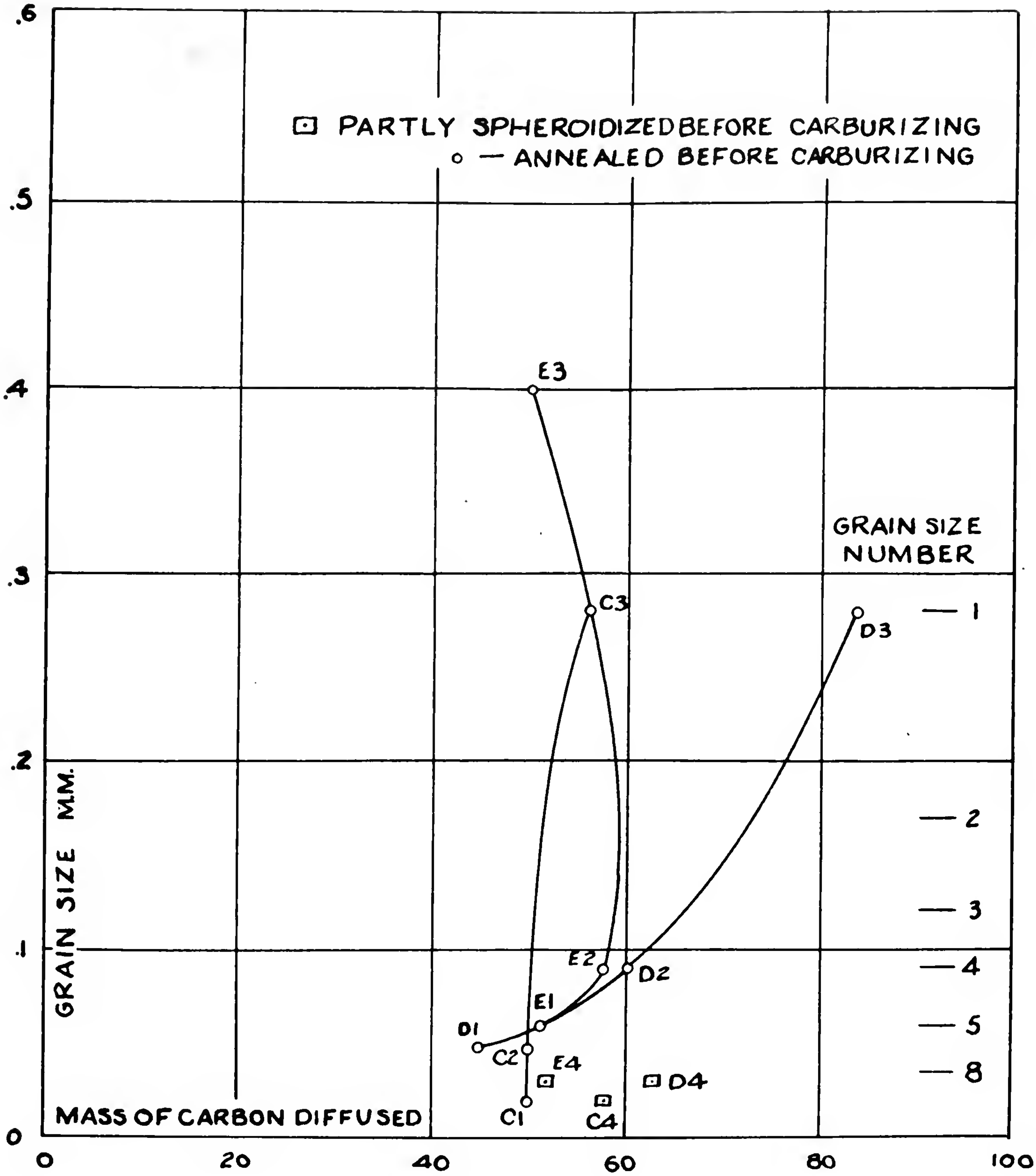


FIGURE 11

COMPARISON OF MASS OF CARBON DIFFUSED FOR VARIOUS SAMPLES
STEEL C, D, AND G

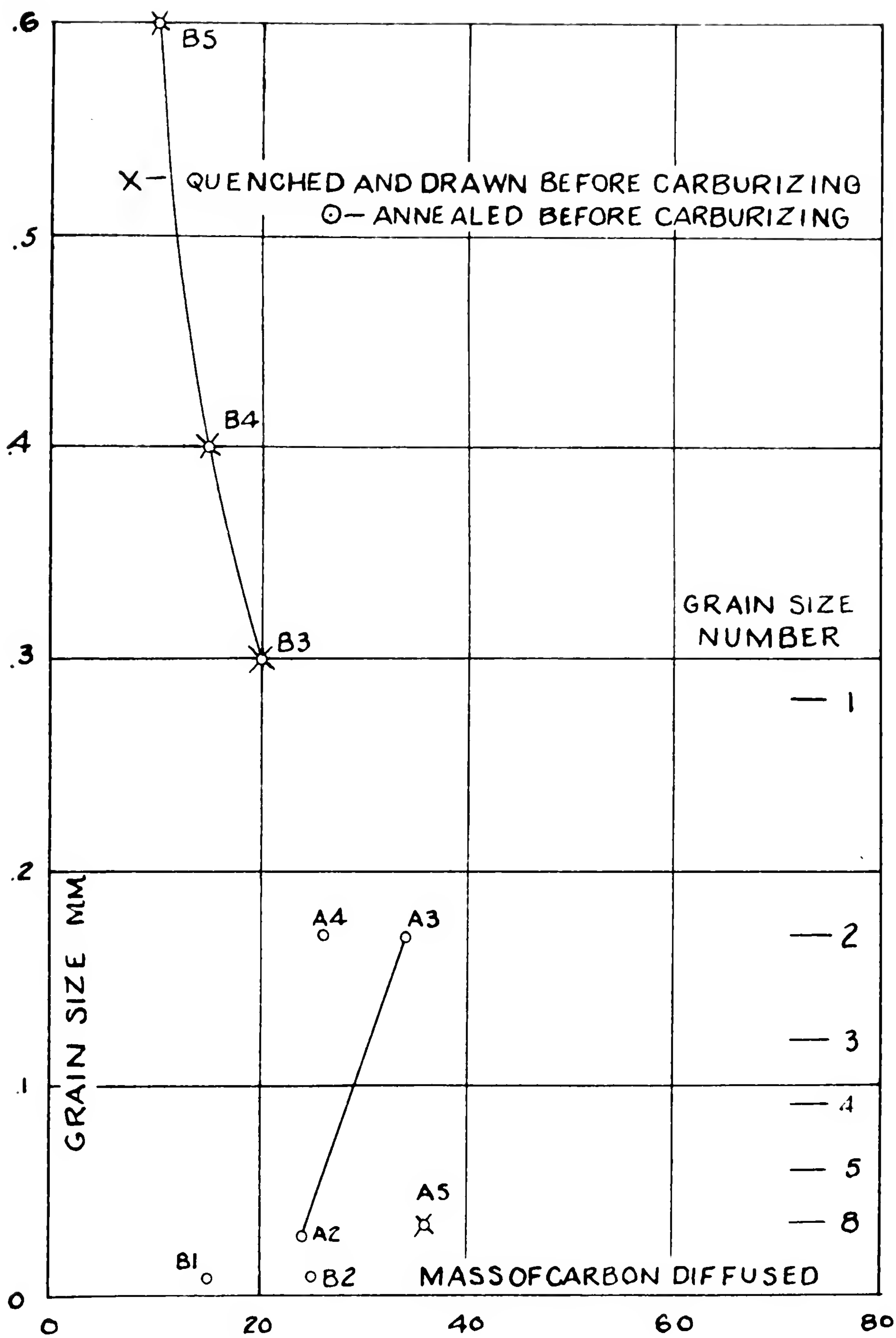


FIGURE 12

COMPARISON OF MASS OF CARBON DIFFUSED FOR VARIOUS SAMPLES STEEL A AND B

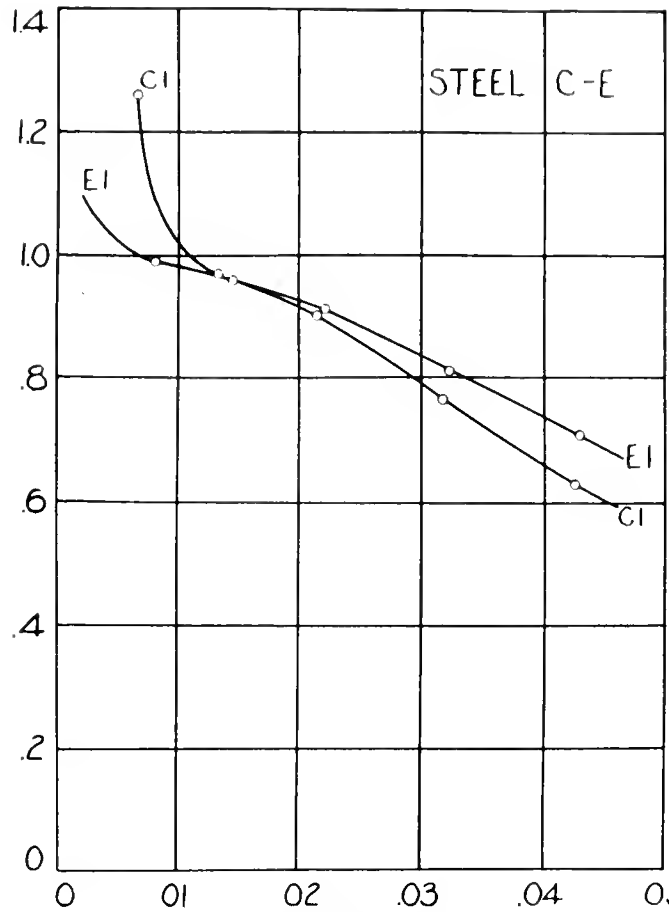


FIGURE 13

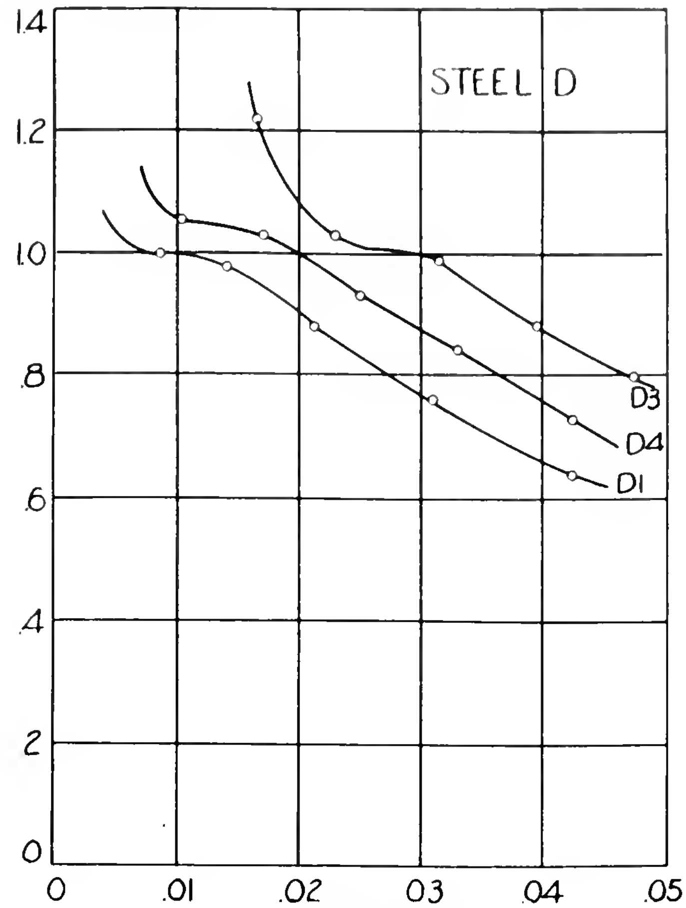


FIGURE 14

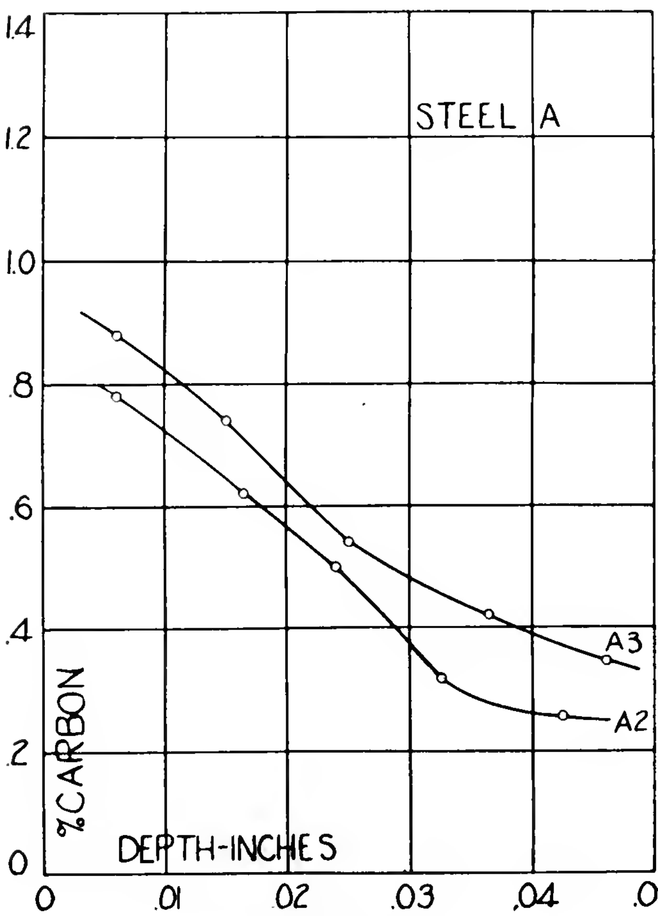


FIGURE 15

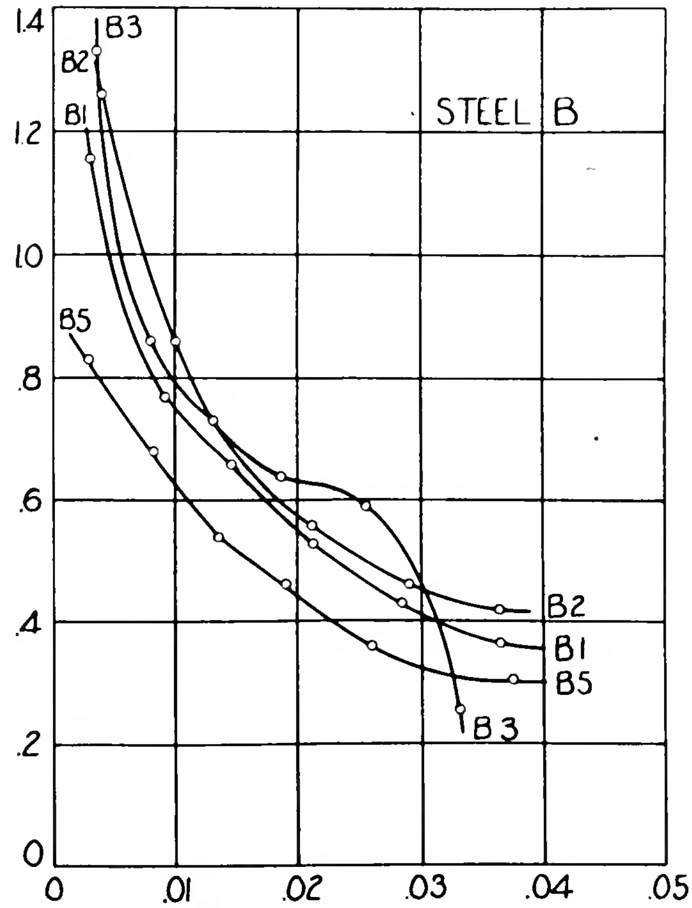


FIGURE 16

CARBON PENETRATION CURVES
CARBON CONCENTRATION PLOTTED AGAINST DEPTH

Table I.

Compositions of steels under test.

Sample no.	SAE no.	Carbon %	Manganese %	Nickel %	Chromium %	Molybdenum %
A	1020	0.24	0 .56	-	-	-
B	3335	0.34	0.33	3.79	1.72	-
C	3335	0.355	0.48	3.41	1.45	-
D	4335	0.37	0.73	1.75	0.73	0.37
E	3435	0.415	0.47	2.95	0.76	-

Table I.

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A	1020	0.24	0.56	-	-	-
B	3335	0.34	0.33	2.79	1.72	-
C	2335	0.355	0.48	3.41	1.45	-
D	4335	0.37	0.73	1.75	0.73	0.27
E	3435	0.415	0.47	2.95	0.75	-

Table II.

Histories of individual samples.

Sample no.	Preliminary treatment Heat to °F	for hours	Manner of cooling	Grain size before carburizing mm.	No.	Relative mass of carbon diffused during carb.
A1	1800	3	box cooled	0.02	8	24. (estimated from appearance)
A2	1800	3	" "	0.03	7	24.2
A3	2100	3	" "	0.17	2	34.4
A4	2100	20	" " (oxidized)	0.17	2	27.2
A5	1800	2	water quenched	-	-	36.6
A6	2100	2	" "	-	-	35 (estimated by appearance)
B1	as received, drawn at 1200 ½ hr.			0.01	8	15.4
B2	1630	2	cooled in sand	0.01	8	24.2
B3	2450	10 and				
	2150	1	box cooled	0.3	1	19.7
B4	2450	10 and				
	1850	2	box cooled	0.4	1	15.0
B5	2500	1	box cooled	0.6	1	9.8
B6	2100	1	air cooled	0.2	2	9.1 (blued spot after barb.)
C1	1600	2	furnace cooled	0.02	8	49.7
C2	1850	2	"	0.05	6	49.8
C3	2100	2	"	0.28	1	55.4
C4	1300	22	"	0.02	8	57.2
D1	1600	2	"	0.05	6	44.8
D2	1850	2	"	0.09	4	60.3
D3	2100	2	"	0.28	1	84.0
D4	1300	22	"	0.03	7	62.7
E1	1600	2	"	0.06	5	52.0
E2	1850	2	"	0.09	4	57.9
E3	2100	2	"	0.4	1	49.5 (blued spot after carb.)
E4	1300	22	"	0.03	7	51.3

Table II.

Histories of individual samples.

Sample no.	Preliminary treatment: Heat to °F	for hours	Manner of cooling	Grain size before carburizing mm.	No.	Relative mass of carbon diffused during carb.	
A1	1800	3	box cooled	0.02	No. 8	24.	(estimated from appearance)
A2	1800	3	" "	0.03	7	24.2	
A3	2100	3	" "	0.17	2	34.4	
A4	2100	20	" " (oxidized)	0.17	2	27.2	
A5	1800	2	water quenched	–	–	25.6	
A6	2100	2	" "	–	–	35	(estimated by appearance)
B1	as received, drawn at 1200 ½ hr.			0.01	8	15.4	
B2	1650	2	cooled in sand	0.01	8	24.2	
B3	2450	10 and					
	2150	1	box cooled	0.3	1	19.7	
B4	2450	10 and					
	1850	2	box cooled	0.4	1	16.0	
B5	2500	1	box cooled	0.6	1	9.8	
B6	2100	1	air cooled	0.2	2	9.1	(blued spot after carb.)
C1	1800	2	furnace cooled	0.02	8	49.7	
C2	1850	2	"	0.05	6	49.8	
C3	2100	2	"	0.28	1	55.4	
C4	1300	22	"	0.02	8	57.2	
D1	1600	2	"	0.05	6	44.8	
D2	1850	2	"	0.09	4	50.6	
D3	2100	2	"	0.28	1	64.0	
D4	1300	22	"	0.03	7	62.7	
E1	1600	2	"	0.06	5	52.0	
E2	1850	2	"	0.09	4	57.9	
E3	2100	2	"	0.4	1	49.5	(blued spot after carb.)
E4	1300	22	"	0.03	7	51.6	

Table III.

Data on steels under test

Steel no.	Critical points Ac3	Critical points Ac1	Carbon percentage of Eutectoid %	Carburizing Temp. °F	Carburizing Time hrs.	Difference between Ac3 and carb. temperature	Effect of initial grain size
A	1575	1337	0.82	1635	12	60	yes
B	1350	1345	0.47	1465	"	115	yes
C	1350	1345	0.50	1615	"	265	none
D	1450	1360	0.61	1615	"	165	yes
E	1360	1320	0.60	1615	"	255	none

Table IV

Averaged results of carburizing tests.

Samples		Relative mass of carbon diffused #	Remarks.
A	(all)	30.6	Similar composition
B	"	16.8	"
C	"	53.0	"
D	"	63.0	"
E	"	52.7	"
C1 D1 E1		53.9	Similar treatment
C2 D2 E2		61.6	"
C3 D3 E3		73.2	"
C4 D4 E4		61.7	"

Steels C,D,E - carburized at one time

To convert relative mass of carbon to absolute mass in pound per hour per square inch of exposed surface, multiply by 5.9x.513

Table III.

Data on steels under test

Steel no.	Critical points Ac3	Ac1	Carbon percentage of Eutectoid %	Carburizing Temp. °F	Time hrs.	Difference between Ac3 and carb. temperature	Effect on initial grain size
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B	1350	1345	0.47	1465	"	115	yes
C	1350	1345	0.30	1615	"	265	none
D	1450	1360	0.61	1615	"	165	yes
E	1360	1320	0.60	1615	"	255	none

Table IV

Averaged results of carburizing tests.

Samples		Relative mass of carbon diffused #	Remarks.	
A	(all)	30.6	Similar composition	
B	"	18.8	"	Steels C,D,E - carburized at one time
C	"	53.0	"	
D	"	63.0	"	
E	"	52.7	"	
C1 D1 E1		53.9	Similar treatment	
C2 D2 E2		61.6	"	
C3 D3 E3		72.2	"	
C4 D4 E4		51.7	"	

To convert relative mass of carbon to absolute mass in pound per hour per square inch of exposed surface, multiply by 5.9x.513

I. BIBLIOGRAPHY

1. On rates of reactions in solid steel — by . C. Bain.
Transactions of the
American Institute of Mining and Metallurgical Engineers,
Vol. 13, page 100, year 1932.

2. Grain Size and Grain Growth — by M. A. Grossman
Transactions of the American Society for Steel Treating,
Vol. 21, page 1079, year 1933.

3. Grain Growth in Metals — by M. A. Grossman
Transactions of the American Society for Metals,
Vol. 22, page 861, year 1922.

4. Grain size and Hardenability and Normality of Steels — by E.S. Davenport, and E.C. Bain.
Transactions of the American Society for Metals,
Vol. 22, page 879, 1922.

5. Grain Size and Its Influence on Surface Decarburization of Steel — by P.H. Rowland, and C. Upthegrove.
Transactions of the American Society for Metals,
Vol. 24, page 96, 1936.

6. Sonder Stahlkunde, 1935, pages 68-75, — E. Houdremont

7. Influence of Lattice Distortion on Diffusion in Metals, — by V.G. Mooradian and J. T. Norton
Transactions of the American Institute of Mining and Metallurgical Engineers,
Vol. 117, page 89, 1935.

8. Thoriated Tungsten Filaments — by I. Langmuir
J. Franklin Institute, Vol. 217, page 543, 1934.

9. The Mechanism of Crystal Growth — by W. P. Davey
Transactions of the American Societyfor Steel Treating,
Vol. 21, page 965, 1933.

10. Cementation Des Produits Metallurgiques,
L. Guillet, p.1-29, 53-65.

11. The Role of Energizers in Carburizing Compounds by G. M. Enos,
Transactions of the American Society for Steel Treating,
Vol. 20, page 27, 1932.

12. Continuous gas Carburizing in Practice. — by E. A. Thomas
Metals and Alloys, Vol. 3, page 84, 1932.

[illegible]

1. On rates of reactions in solid steel, by [illegible]
Transactions of the American Institute of Mining and Metallurgical Engineers, Vol. [illegible], [illegible], year [illegible].

2. Grain Size and [illegible], by [illegible]
Transactions of the American Society for Steel Treating, Vol. 21, page 107, year [illegible].

3. Grain Growth in Metals, by [illegible]
Transactions of the American Society for Metals, Vol. [illegible], page [illegible], year [illegible].

4. Grain size and Hardenability and Normality of Steels, by [illegible] Davenport, and [illegible] Bain.
Transactions of the American Society for Metals, Vol. 22, page [illegible], [illegible].

5. Grain Size and Its Influence on Surface Decarburization of Steel, by [illegible], and [illegible].
Transactions of the American Society for Metals, Vol. 24, page 65, [illegible].

6. Schneider, [illegible], 1935, pages 58-75, [illegible]

7. Influence of Lattice Distortion on Diffusion in Metals, by [illegible] and [illegible] Norton
Transactions of the American Institute of Mining and Metallurgical Engineers, Vol. 117, page 53, [illegible].

8. Thoriated Tungsten Filaments, by I. Langmuir
J. Franklin Institute, Vol. [illegible], page [illegible], [illegible].

9. The Mechanism of Crystal Growth, by [illegible] Davey
Transactions of the American Society for Steel Treating, Vol. 21, page [illegible], [illegible].

10. Cementation Des Produits Metallurgiques, L. Guillet, [illegible].

11. The Role of Energizers in Carburizing Compounds by [illegible],
Transactions of the American Society for Steel Treating, Vol. 20, page 27, [illegible].

12. Continuous gas Carburizing in Practice, by [illegible] A. Thomas
Metals and Alloys, Vol. 5, page 84, [illegible].

13. Effect of Alloying Elements Upon Behavior of Steels in Case-hardening, (Einflub DRR Legierungselemente Auf Des Verhalten Von Stahlen Bei Der Einsatzhartung) by Von E. Houdremont and H. Schrader, Arch. Eisenhuttenw. Vol. 8, page 445, 1935.

14. Steel For Case-Hardening - Normal and Abnormal Steel, by S. Epstein and H. S. Rawdon Bureau Standards Journal of Research, Vol. 1, page 423, 1928.

15. The Effects of McQuaid-Ehn Grain Size on the Structure and Properties of Steel by P. Shand, Jr. Transactions of the American Society for Metals, Vol. 22, page 1038, 1932.

16. Heat treatment in Controlled Atmospheres Including Gaseous Carburizing, by C. R. Austin, Transactions of the American Society of Metals, Vol. 23, pages 168-170, 1935.

17. The Metallography and Heat Treatment of Iron and Steel, by A. Sauveur, Fourth Edition, pp. 312-317.

18. Influence of special Elements on the Content of the Iron Carbon Eutectoid, by E. L. Reed, Transactions of the American Society for Steel Treating, Vol. 20, page 115, 1932.

19. Submicroscopic Inclusions in Steel, by C. H. Herty Metal Progress Vol. 20-4, p. 37, or Transactions of the American Society for Steel Treating, Vol. 19, page 1, 1931.

20. Abnormality in Case Carburized Steels, by Herty, Larson, Krivobok, and co-workers. Mining & Metallurgical Cooperative Bulletin No. 45, 1929.

21. National Metals Handbook, 1933 American Society for Metals, pp. 350, 650, 907, 920.

22. Diffusion in Solid Metals, by R. F. Mehl, Annual Lecture before American Institute of Mining and Metallurgical Engineers' meeting in New York in February 1936, and to be published by the Institute of Metals Division of that Society.

23. The Effect of McQuaid-Ehn Grain Size on Hardness and Toughness of Automotive Steels, by H. W. McQuaid, Transactions of the American Society for Metals, Vol. 22, page 1017, 1934.

13. Effect of Alloying Elements Upon [illegible] of Steels in Case-hardening
(Einfluss der Legierungselemente auf [illegible] von Stählen bei der Einsatzhärtung) — by [illegible] and H. [illegible]
Arch. Eisenhüttenw. Vol. 9, page 4[illegible], 1936.

14. Steel for Case-hardening — [illegible] Steel, — by [illegible] and [illegible]
Bureau of Standards Journal of Research, Vol. 1, page 4[illegible], 1928.

15. The Effects of McQuaid-Ehn Grain Size on the Structure and Properties of Steel — by [illegible], Jr.
Transactions of the American Society for Metals,
Vol. 23, page 10[illegible], 1935.

16. Heat treatment in Controlled Atmospheres Including Gaseous Carburizing, — by [illegible]
Transactions of the American Society of Metals,
Vol. 22, pages 1[illegible], 1934.

17. The Metallography and Heat Treatment of Iron and Steel, — by A. Sauveur,
Fourth Edition, pp. 313-317.

18. Influence of Special Elements on the Content of the Iron Carbon Eutectoid, — by [illegible] L. Reed,
Transactions of the American Society for Steel Treating,
Vol. 20, page 115, 1932.

19. Submicroscopic Inclusions in Steel, — by C. H. Herty
Metal Progress Vol. 20-4, p. 37, or
Transactions of the American Society for Steel Treating,
Vol. 19, page 1, 1931.

20. Abnormality in Case Carburizing Steels, — by Herty, Larson,
Mining & Metallurgical Cooperative — Privoznik, and co-workers
Bulletin No. 46, 1929.

21. National Metals Handbook, 1933
American Society for Metals, pp. [illegible], 980, 809, [illegible].

22. Diffusion in Solid Metals, — by R. F. Mehl,
Annual Lecture before American Institute
of Mining and Metallurgical Engineers'
meeting in New York in February 1936, and
to be published by the Institute of Metals
Division of that Society.

23. The Effect of McQuaid-Ehn Grain Size on Hardness and Toughness of Automotive Steels, — by H. W. McQuaid,
Transactions of the American Society for Metals,
Vol. 22, page 1017, 1934.

24. Gas Carburizing - a Discussion of Shop Practices, by H.W. McQuaid
Metal Progress (July 1934) p. 23.

25. Versuche Uber Die Diffusion von Kohlenstoff, Silizium, und Mangan in Festem und Flussigem Eisen, Arch. Eisenhutenw. Vol. 9, pp. 305-6, 1935. by Von M. Paschke, and A. Hauttmann,

26. The Gaseous Cementation of Iron and Steel, Part 1, Carnegie Scholarship Memoirs, Vol. 15, page 17, 1926. by A. Bramley and A. J. Jinkings,

27. The Gaseous Cementation of Iron & Steel, Part 2, Carnegie Scholarship Memoirs, Vol. 15, page 71, 1926. by A. Bramley and G. H. Beeby,

28. The Gaseous Cementation of Iron & Steel, Pt. IV, by A. Bramley and G. Turner, Carnegie Scholarship Memoirs, Vol. 17, page 23, 1928.

29. The Gaseous Cementation of Iron & Steel, Part VI, Carnegie Scholarship Memoirs, Vol. 18, page 1, 1929. by A. Bramley and H. D. Lord,

24. Gas Carburizing - a Discussion of [illegible]
Metal Progress (July 193[illegible]) p. [illegible]

25. Versuche über die Diffusion [illegible]
und Kupfern in Eisen und Flusseisen [illegible] [illegible] and A. [illegible]
Arch. Eisenhütten.
Vol. 9, pp. [illegible]

26. The Gaseous Cementation of Iron and Steel, Part I. by [illegible] and
Carnegie Schol. Memoirs, [illegible] Jinnings,
Vol. 15, page [illegible], 1926.

27. The Gaseous Cementation of Iron [illegible] by [illegible] Bramley and
Carnegie Schol. Memoirs, [illegible]
Vol. 15, page [illegible], 1926.

28. The Gaseous Cementation of Iron & Steel, [illegible] by [illegible] Bramley and
Carnegie Schol. Memoirs, [illegible]
Vol. 17, page [illegible], 1928.

29. The Gaseous Cementation of Iron & Steel, Part II, by [illegible] Bramley and
Carnegie Schol. Memoirs, [illegible] Lord,
Vol. 18, page 1, [illegible].